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SOLID HYDROGENATION CATALYST FOR UNSATURATED ALDEHYDE AND METHOD OF
HYDROGENATION OF UNSATURATED ALDEHYDE USING THE SAME
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1. Title of the Invention

SOLID HYDROGENATION CATALYST FOR UNSATURATED ALDEHYDE AND METHOD OF HYDROGENATION OF UNSATURATED ALDEHYDE USING THE SAME

2. Claims

1. A solid hydrogenation catalyst for an unsaturated aldehyde comprising platinum oxide and an iron compound and zinc compound which are deposited on said platinum oxide surface under an atmosphere of hydrogen.

2. The solid hydrogenation catalyst for unsaturated aldehyde as described in Claim 1, wherein said solid catalyst has a surface area of 10 ~ 60 m²/g and the amounts of the iron compound and the zinc compound present in a skin layer having a depth of 1 μ from the surface of said solid catalyst, are, converted to metallic iron and zinc, 1.5 ~ 70 weight% and 0.5 ~ 8 weight%, respectively, based on the sum of platinum oxide, the iron compound and the zinc compound, which are converted to their metals.

3. The solid catalyst as described in Claim 1, wherein the amounts of the iron compound and the zinc compound present in a skin layer having a depth of 1 μ from the surface of said solid catalyst are, converted to metallic iron and zinc, 1.5 ~ 50 weight% and 2.5 ~ 7 weight%, respectively, based on the sum of platinum oxide, the iron compound and the zinc compound, which are converted to their metals.

4. The solid catalyst as described in Claim 1, wherein said iron compound is an inorganic acid salt or an organic acid salt of iron.

*Numbers in the margin indicate pagination in the foreign text.

5. The solid catalyst as described in Claim 4, wherein said iron is divalent or trivalent iron.

6. The solid catalyst as described in Claim 4, wherein said iron compound is ferrous sulfate or ferrous acetate.

7. The solid catalyst as described in Claim 1, wherein said zinc compound is an inorganic acid salt or an organic acid salt of zinc.

8. The solid catalyst as described in Claim 7, wherein said zinc compound is zinc sulfate or zinc acetate.

9. The solid catalyst as described in Claim 1, wherein said solid catalyst has a surface area of $12 \sim 50 \text{ m}^2/\text{g}$.

10. The solid catalyst as described in Claim 1, wherein said solid catalyst has a agglomerate form with an average particle size of $10 \sim 100$ microns.

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11. The solid catalyst as described in Claim 1, wherein said solid catalyst is prepared by bring the iron compound and the zinc compound into contact with platinum oxide simultaneously or in a desired order in an inert organic solvent under an atmosphere of hydrogen.

12. The solid catalyst as described in Claim 11, wherein the partial pressure of said hydrogen is in the range of $0.1 \sim 300 \text{ kg/cm}^2$.

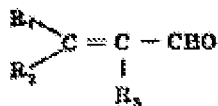
13. The solid catalyst as described in Claim 11, wherein said inert organic solvent is a lower aliphatic alcohol.

14. A method of manufacturing an unsaturated alcohol by the catalytic hydrogenation of the corresponding unsaturated aldehyde in the presence of a solid hydrogenation catalyst, wherein said solid catalyst comprises

platinum oxide and the iron compound and the zinc compound which are deposited on the surface of said platinum oxide under an atmosphere of hydrogen.

15. The method as described in Claim 14, wherein said solid catalyst has a surface area of $10 \sim 60 \text{ m}^2/\text{g}$ and the amounts of the iron compound and the zinc compound present in a skin layer having a depth of 1μ from the surface of said solid catalyst are, converted to metallic iron and zinc, $1.5 \sim 70 \text{ weight\%}$ and $0.5 \sim 8 \text{ weight\%}$, respectively, based on the sum of platinum oxide, the iron compound and the zinc compound, which are converted to their metals.

16. The method as described in Claim 14, wherein said unsaturated aldehyde is α, β -unsaturated aldehyde as shown by the formula below:



(wherein in the above formula, R_1 represents a saturated or unsaturated hydrocarbon group; R_2 and R_3 are the same or different and independently represent a hydrogen atom, a saturated or unsaturated hydrocarbon group or a heterocyclic group).

17. The method as described in Claim 14, wherein said catalytic hydrogenation is carried out at a temperature in the range of $-40 \sim 300^\circ\text{C}$.

18. The method as described in Claim 14, wherein said catalytic hydrogenation is carried out repeatedly by a batch method or a continuous method in the presence of a recycling same solid catalyst, and in the above

process, an iron compound and a zinc compound are added to said recycling solid catalyst in amounts of, converted to metallic iron and zinc, 0.0002 ~ 0.03 weight parts and 0.0002 ~ 0.004 weight parts, respectively, per 1 weight part of platinum oxide.

3. Detailed explanation of the invention

The present invention relates to a novel catalyst composition. Explaining in more detail, the present invention relates to a solid catalyst comprising platinum oxide and an iron compound and a zinc compound which are deposited on the surface of platinum oxide under an atmosphere of hydrogen, and a method of manufacturing an unsaturated alcohol by the selective hydrogenation of an unsaturated aldehyde using the above solid catalyst.

In hydrogenation of an unsaturated aldehyde, normally the unsaturated bond is more susceptible to hydrogenation than the aldehyde group. Therefore, in selective hydrogenation of an aldehyde group to form the corresponding unsaturated alcohol, special hydrogenation conditions are required.

Conventionally, as a method of selective hydrogenation of an unsaturated aldehyde to form the corresponding unsaturated alcohol, the use of platinum oxide as a hydrogenation catalyst, in addition to iron and/or zinc salt which are present in the reaction system has been disclosed [e.g. refer to R. Adams and B.S. Garvey, J. Am. Chem. Soc., 48, 477 (1926); P.N. Rylander, N. Himelstein and N. Kilroy, Engelhard Ind. Tech. Bull., 4, 49 (1963)].

However, in the above conventional method, it is difficult to separate the catalyst from the reaction product, requiring a long time for the separation. Even after separation, the above solid catalysts remain in the reaction product in a colloidal form, which are difficult to remove by a normal separation method. Furthermore, in the reaction product, not only platinum, but also a large amount of the iron compound and the zinc compound remain dissolved in the reaction product. When such a reaction product is subjected to a distillation separation, an undesirable side reaction of the formed unsaturated alcohol and/or unreacted /3
unsaturated aldehyde takes place, causing extremely poor yield of the desired alcohol and poor recovery of the unreacted aldehyde. Furthermore, when the unsaturated alcohol is continuously manufactured by repeated use of the above catalysts, the degree of selectivity for a desired alcohol becomes deteriorated within a very short period of time, causing extremely poor yield of the unsaturated alcohol. Therefore, the above method is entirely unsatisfactory from the industrial standpoint.

The purpose of the present invention is to provide a novel catalyst based on 3 components, a platinum oxide, an iron compound and a zinc compound which does not have above disadvantages.

Another purpose of the present invention is to provide a solid catalyst for hydrogenation of unsaturated aldehyde, which can be easily separated from the reaction product, exhibits a high degree of selectivity for unsaturated alcohol and can maintain a high degree of selectivity for

unsaturated alcohol for a long time even when it is used repeatedly and continuously.

Still another purpose of the present invention is to provide a method of manufacturing an unsaturated alcohol from the corresponding unsaturated aldehyde by selective hydrogenation of the aldehyde group using the above novel catalyst.

The other purposes and the advantages of the present invention will be manifested from the detailed explanation of the present invention as described below.

The present invention provides a solid catalyst based on platinum oxide and an iron compound and a zinc compound which are deposited on the surface of platinum oxide under an atmosphere of hydrogen.

The essential difference between the above-mentioned conventional catalyst and the catalyst of the present invention is that in the catalyst of the present invention, the iron compound and the zinc compound are pre-deposited on the surface of platinum oxide under an atmosphere of hydrogen.

The solid catalyst of the present invention based on platinum oxide prepared under an atmosphere of hydrogen has the following excellent industrial advantages: since the adhesion of the iron compound and the zinc compound to the surface of the platinum oxide substrate is strong, the degree of elution of the iron compound and the zinc compound into the reaction mixture is low; and since the catalyst is easily agglomerated to form a stable particle with an appropriate particle size, the catalyst

can be easily recovered from the reaction product in a short period of time at a high yield after the completion of the reaction. Furthermore, the solid catalyst of the present invention has another excellent advantage in that when this catalyst is used in the manufacture of an unsaturated alcohol by the hydrogenation of the corresponding unsaturated aldehyde, it exhibits an extremely high degree of selectivity for unsaturated alcohol as compared to the conventional solid catalyst and maintains its high degree of selectivity for a long time even during repeated use.

The solid catalyst of the present invention comprises the iron compound and the zinc compound which are deposited on the surface of the platinum oxide base. Its surface area is $10 \sim 60 \text{ m}^2/\text{g}$, or preferably $12 \sim 50 \text{ m}^2/\text{g}$. In the description of the present invention, "the surface area" is obtained by the BET method, which is conventionally used in the measurement of the surface area of a solid catalyst. The measurement was carried out using a "Sorptometer 21 D type" from Perkin-Elmer Co. and expressed as the surface area (m^2) per unit solid catalyst (g).

In the solid catalyst of the present invention, as platinum oxide used as a base, any grades which are conventionally used as the hydrogenation catalyst can be used. For example, the so-called Adams-type platinum oxide can be preferably used, [For example, refer to "Organic Synthesis", col., 1, 463 (1948)]. Also, its size is preferably in the range of $1 \sim 3$ microns.

As iron compounds and zinc compounds which can be deposited on the surface of platinum oxide, those which are at least partially soluble in

the inert organic solvent to be used in the catalyst preparation, which will be described below, are preferable. For example, inorganic acid salts [for example, a sulfate, a nitrate, a phosphate, a halide (e.g. a chloride), a carbonate and the like], or organic acid salts [for example, lower ($C_1 \sim C_4$) aliphatic mono- or di-carboxylic acids such as an acetate, a formate, a oxalate and the like] of iron and zinc are preferable. In particular, sulfates or acetates of iron and zinc are preferable.

The valency of iron in the above iron compounds may be any number, 1, 2, 3, 4, or 5. In particular, a valency of 2 or 3 is preferable, or a valency of 2 is more preferable. As the iron compound, iron sulfate or iron /4 acetate is preferable.

Zinc in the zinc compound exists as a valency of 2. As the zinc compound, zinc sulfate or iron [sic. Translator's note: should be "zinc"] acetate is preferable.

It is advantageous that the amount of the iron compound and zinc compound to be deposited on the surface of platinum oxide is such that the ratios of platinum oxide, the iron compound, and the zinc compound which exist in the skin layer with a depth of 1 micron from the surface of the solid catalyst of the present invention are, converted to the weight of each metal, 1.5 ~ 70 weight%, or preferably 1.5 ~ 50 weight% for iron, 0.5 ~ 8 weight%, or preferably 2.5 ~ 7 weight% for zinc, and accordingly 98.0 ~ 22 weight%, or preferably 96 ~ 43 weight% for platinum, based on the total weight of these compounds converted to corresponding metals. The amounts of the deposited iron compound and zinc compound in the

description of the present invention are calculated according to the method as describe below.

That is, using a X-ray analyzer [Electron Mycroprobe [sic.] X-ray Analyzer 2A type from Shimazu-ARL Co.], platinum oxide, the iron compound and the zinc compound which were present in the skin layer with a thickness of 1 micron from the surface of the solid catalyst were measured according to the conditions as shown below.

Accelerating Voltage : 30 KV
 Sample Current : 0.0013 AA
 Take off Angle of X -- Rays from Sample Surface : 52.5°
 Dispersible Crystal : LIF
 Detector : Kr -- Electron
 X -- Ray Diameter : 2 μm
 Sample Speed : 9.6 μm/mm
 Used X -- Rays : Fe Kα 1.937 Å
 Zn Kα 1.436 Å
 Pt Lα 1.313 Å

Based on the amounts of platinum oxide, the iron compound and the zinc compound obtained from the above measurement, the iron retention and the zinc retention were obtained according to the following definitions.

The iron retention (X) = (the weight of converted iron metal) x 100/(the total weight of converted platinum, iron and zinc metals)

The zinc retention (Y) = (the weight of converted zinc metal) x 100/(the total weight of converted platinum, iron and zinc metals)

The solid catalyst of the present invention can be prepared by, for example, bringing the iron compound and the zinc compound into contact

with platinum oxide simultaneously or in a desired order in an inert organic solvent under an atmosphere of hydrogen.

As the inert organic solvent which can be used in the present invention, although any solvent can be used as long as it is stable under an atmosphere of hydrogen, it is convenient to use the same solvent as used in the hydrogenation reaction, in which the solid catalyst of the present invention is used, from the practical standpoint. Normally, lower ($C_1 \sim C_4$) aliphatic alcohols, such as methanol, ethanol and the like are preferably used.

The important point in preparation of the catalyst of the present invention is that contacting of platinum oxide with the iron compound and the zinc compound is to be carried out under an atmosphere of hydrogen.

The present inventors have discovered that when the solid catalyst is prepared by first treating platinum oxide under an atmosphere of hydrogen until the adsorption of hydrogen ceases, then depositing the iron compound and the zinc compound to the surface of this treated platinum oxide, the resultant solid catalyst does not exhibit excellent properties even when the deposition process is carried out under an atmosphere of hydrogen. However, the present inventors have surprisingly discovered that when the solid catalyst is prepared by bring the iron compound and the zinc compound into contact with an untreated platinum oxide under an atmosphere of hydrogen, the resultant solid catalyst has various advantages as described above.

That is, the above catalyst is prepared under an atmosphere of hydrogen, in which the hydrogen partial pressure is generally in the range

of $0.1 \sim 300 \text{ kg/cm}^2$, or preferably $0.2 \sim 200 \text{ kg/cm}^2$. In this case, hydrogen can exist in a pure form, or as a mixture with an inert gas, such as nitrogen, carbon dioxide gas, helium, argon and the like.

Also, although the catalyst can be prepared at a wide temperature range, it is preferably carried out at $-40 \sim 200^\circ\text{C}$, or more preferably at $-10 \sim 150^\circ\text{C}$, or even more preferably at room temperature. Although the reaction time varies depending on the type or the amount of iron compound and the zinc compound to be used, it is normally in the range of 1 minute \sim 10 hours.

The catalyst preparation can be carried out, for example, by suspending platinum oxide in an inert organic solvent as described above and adding the iron compound and the zinc compound simultaneously, in /5 that order, or a reverse order to bring these compounds into contact with platinum oxide under an atmosphere of hydrogen. When the iron compound and the zinc compound are to be added in sequence, for example, the iron compound is added first and it is sufficiently brought into contact with platinum oxide under an atmosphere of hydrogen. Then, the zinc compound is added next, and it is sufficiently brought into contact with the previously treated platinum oxide under an atmosphere of hydrogen.

In preparation of the catalyst, the iron compound can be added in an amount of, converted to the metallic iron, $0.04 \sim 0.8$ weight parts per 1 weight part of platinum oxide, or preferably $0.04 \sim 0.5$ weight parts. The zinc compound can be added in an amount of, converted to the metallic

zinc, 0.01 ~ 0.3 weight parts per 1 weight part of platinum oxide, or preferably 0.01 ~ 0.2 weight parts.

The obtained solid catalyst of the present invention comprises a platinum oxide base to which the iron compound and the zinc compound adhere strongly. It has an average particle size of normally in the range of 10 ~ 100 microns and exists in an agglomerate form, exhibiting excellent sedimentation property in the reaction mixture.

As a result, the obtained solid catalyst can be isolated by conventional separation methods, such as a sedimentation separation, centrifugation, filtration and other methods. The separated catalyst can be washed, as necessary, with an appropriate solvent, such as the solvent which is used in the preparation of the catalyst or the solvent which is used in the hydrogenation reaction using the catalyst of the present invention as will be described below. Or, it can be used without washing in the next step, which will be described below, after drying or without drying.

The catalyst of the present invention can be used as a selective hydrogenation catalyst for the aldehyde group in an unsaturated aldehyde in the manufacture of the corresponding unsaturated alcohol.

Therefore, the present invention provides a novel and improved solid catalyst in the manufacture of an unsaturated alcohol by the catalytic hydrogenation of an unsaturated aldehyde using hydrogen in the presence of a solid hydrogenation catalyst.

The unsaturated aldehyde, which can be hydrogenated using the catalyst of the present invention, is an organic compound which has at least 1 unsaturated bond and at least 1 aldehyde (CHO) group. It can be an aliphatic, aromatic, alicyclic, or heterocyclic unsaturated aldehyde. Furthermore, the above unsaturated aldehyde may have an inert atom or a group which does not participate in the hydrogenation reaction in a molecule, such as a hydroxyl group, amino group, halogen atom and the like.

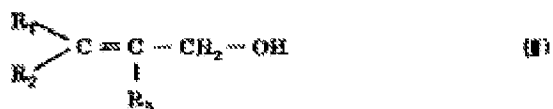
As described above, the catalyst of the present invention is quite appropriate as a hydrogenation catalyst for selective hydrogenation of the aldehyde group (CHO) to convert to the hydroxymethyl group (CH₂OH). For example, even for an unsaturated aldehyde having the α,β -unsaturated group in a molecule which is highly susceptible to reduction, the catalyst of the present invention can selectively reduce only the aldehyde group to give the corresponding unsaturated alcohol at a high degree of selectivity and a high degree of conversion.

The catalyst of the present invention is quite appropriate in hydrogenation of an α,β -unsaturated aldehyde as shown by the formula below:



(wherein in the above formula, R₁ represents a saturated or unsaturated hydrocarbon group; R₂ and R₃ are the same or different and independently represents a hydrogen atom, a saturated or unsaturated hydrocarbon group

or a heterocyclic group) to convert to an α,β -unsaturated alcohol as shown by the formula below:



(wherein in the above formula, R_1 , R_2 and R_3 have the same meaning as above).

A preferred α,β -unsaturated aldehyde of the present invention has R_1 , R_2 and R_3 which have a carbon number not exceeding 50, or preferably not exceeding 30 and which are preferably selected from an alkyl group, alkenyl group, alkynyl group, alicyclic group, aromatic group, a /6 group in which at least 2 of these groups are bonded, or a heterocyclic group in which at least 2 of these groups are bonded through oxygen, sulfur, or nitrogen. Among those groups, those whose carbon number does not exceed 50, and preferably does not exceed 30, and those selected from an alkyl group, alkenyl group, alicyclic group, and aromatic group are particularly preferable.

In this case, at least 1 of R_2 and R_3 may be a hydrogen group. Also, in this case, R_1 , R_2 , and R_3 may have a substituent group. As examples of such substituent group, an alkoxy group whose carbon number does not exceed 5, such as methoxy, ethoxy, n-propoxy, iso-propoxy, butoxy, and pentoxy; an alkoxycarbonyl group whose carbon number does not exceed 6, such as methoxycarbonyl, ethoxycarbonyl, n-propoxycarbonyl, butoxycarbonyl, and pentoxy; or a halogen atom such as chlorine, bromine and the like

can be mentioned. Each of R_1 , R_2 and R_3 may have 1 ~ 3 of the above substituent groups.

The most preferable α,β -unsaturated aldehyde has a formula (I) and/or (II) [sic.] in which R_1 represents an alkyl group with a carbon number of 1 ~ 30 or an alkenyl group with a carbon number of 2 ~ 30 and R_2 and R_3 represent a hydrogen atom or an alkyl group with a carbon number of 1 ~ 5.

Concrete examples of an α,β -unsaturated aldehyde to be used in the present invention will be explained below. However, the present invention will not be restricted to these.

(1) Aliphatic aldehyde;

3-ethyl-butene-2-al-1, 3-propylbutene-2-al-1,
3-butylbutene-2-al-1, 3,3-ethylpropyl-acrolein, 2-ethylhexene-2-al-1,
2-ethylisohexene-2-al-1, 2,6-nonadienal, 2-n-amylcrotonaldehyde,
2-hexylcrotonaldehyde, 2-propylidenenanthaldehyde,
2-octylcrotonaldehyde, citral, diisovaleraldehyde, dihydrocitral,
6-methylcitral, citrylideneacetaldehyde, citrylidenepropionaldehyde,
farnesal, and geranyl geranial,

(2) Alicyclic aldehyde;

cyclocitrylideneacetaldehyde, cyclocitrylidenepropionaldehyde,
methyl ional, ionylideneacetaldehyde, Vitamin A aldehyde, dihydroretinal
and tetrahydroretinal,

(3) Aromatic aldehyde;

Cinnamaldehyde, nuciferal, 2-ethylcinnamaldehyde, 2-isopropylcinnamaldehyde, 2-n-butylcinnamaldehyde, 2-hexylcinnamaldehyde, p-methylcinnamaldehyde, p-methyl-2-ethylcinnamaldehyde, 2-methyl-2-isopropylphenylacrolein, 5-phenyl-2-pentene-1-al and benzylidene citronellal,

(4) Heterocyclic aldehyde;

2-Methyl-3-furfurylacrolein, 2-ethyl-3-furfurylacrolein, 2-propyl-furfurylacrolein, 3-methyl-4-furfurylidene-butylaldehyde, and 5-(2-furfuryl)-3-methyl-2-pentenal.

Among above-mentioned aldehydes, those listed in the above (1) and (2) are preferably used. In particular, aliphatic α,β -unsaturated aldehydes listed in the above (1) are the most appropriate.

The hydrogenation of the above unsaturated aldehydes can be carried out by using conventionally known methods. For example, it is advantageous to carry out the hydrogenation of the present invention at a temperature in the range of $-40 \sim 300^{\circ}\text{C}$, or preferably $10 \sim 200^{\circ}\text{C}$, or more preferably $20 \sim 100^{\circ}\text{C}$.

Also, the partial pressure of hydrogen is preferably in the range of $0.5 \sim 300 \text{ kg/cm}^2$, or more preferably $0.8 \sim 200 \text{ kg/cm}^2$.

Also, hydrogen which can be used in the hydrogenation includes not only pure hydrogen, but also a mixture of hydrogen with an inert gas, /7 such as nitrogen, carbon dioxide gas, argon and the like.

Hydrogen can be brought into contact with an unsaturated aldehyde countercurrently or concurrently.

The reaction of the present invention does not necessarily require a use of the solvent. However, the reaction can be carried out in a solvent as necessary. When the solvent is to be used, that which is inert in the hydrogenation reaction and which can practically dissolve the above-mentioned aldehyde as a starting material is preferably used. For example, a lower ($C_1 \sim C_5$) aliphatic alcohol, such as methanol, ethanol and the like, are preferably used. However, it should be understood that the present invention will not be restricted to those.

Also, the above hydrogenation reaction is preferably carried out in the presence of water. By adding water in an amount not exceeding 20 mol per mol of the above unsaturated aldehyde which is to be used in the reaction, or preferably 0.5 ~ 5 mol, the selectivity for the corresponding unsaturated alcohol can be improved.

The above hydrogenation reaction of the present invention can be carried out by a batch method or a continuous method. In either method, the same solid catalyst can be used repeatedly by recycling. During recycling, a new solid catalyst of the present invention can be further added.

According to the present invention, when the iron compound and the zinc compound are added to the above solid catalyst under recycling in an amount of, converted to the metallic iron and zinc, 0.0002 ~ 0.03 weight parts, or preferably 0.0002 ~ 0.004 weight parts and in an amount of 0.0002

~ 0.004 weight parts or preferably 0.0002 ~ 0.0025 weight parts, respectively, per 1 weight part of platinum oxide in the above solid catalyst, the lifetime of the above solid catalyst can be further extended. For example, it has been found that the solid catalyst maintains a high degree of selectivity and conversion after 30 cycles of repeated use in hydrogenation of the unsaturated aldehyde to form the unsaturated alcohol. The above iron compound and the zinc compound may be added to a solid catalyst which is separated from the reaction system and is to be recycled, or to a solid catalyst which is under recycling in the reaction system.

The hydrogenation of the present invention can be carried out using a suspension method, a fixed bed method, a fluidized bed method, or a moving bed method.

According to the present invention, only the aldehyde group (CHO) in the unsaturated aldehyde starting material is converted to the methylenehydroxyl (CH₂OH) group to obtain the corresponding unsaturated alcohol at a high yield. For example, geraniol and prenol can be manufactured from citral and β -methylcrotonaldehyde, respectively, at a high yield.

Separation and recovery of the desired unsaturated alcohol from the reaction product can be carried out using a conventional method.

For example, after the completion of the reaction, the solid catalyst can be separated from the obtained reaction product using a conventional method at the reaction temperature or after the reaction product is cooled down.

For example, in a sedimentation method, after the completion of the reaction, the reaction product is subjected to a sedimentation treatment in a reactor or after being transferred to another container and the supernatant liquid is separated from the settled solid catalyst. Also, other methods such as a filtration method, a centrifugation method and the like, can be mentioned.

As mentioned above, since the solid catalyst of the present invention has an excellent sedimentation property, the catalyst can be separated almost completely using the above method. However, occasionally, a fine solid catalyst may remain in the reaction mixture. In this case, by repeating the above separation operation several times, the solid catalyst can be practically completely separated.

The reaction product, from which the solid catalyst is separated, can be directly subjected to a purification treatment such as distillation.

However, in some cases, the reaction product may contain an iron compound and/or zinc compound which eluted out of the solid catalyst and/or a solid catalyst which was unable to be separated by the above separation process. When the amounts of the iron compound, zinc compound, and /8 the solid catalyst exceed 100 ppm, 100 ppm, and 10 ppm, respectively, converted to the metallic iron, zinc and platinum, based on the sum of the produced unsaturated alcohol and the unreacted aldehyde in the reaction product, it is advantageous that the concentrations of these compounds are reduced to at least 60 ppm, 60 ppm, and 5 ppm, respectively, using

a method such as adsorption, extraction and the like, before the next purification operation such as distillation.

The distillation can be carried out by the conventionally known method. The temperature during the distillation operation, although it varies depending on the types of the unsaturated alcohol and the unreacted residual unsaturated aldehyde, is normally in the range of 10 ~ 300°C, or preferably 50 ~ 200°C since those alcohols and aldehydes generally have poor stability. The pressure during the distillation may be a normal pressure or reduced pressure. Normally, the distillation is carried out under reduced pressure.

For example, the reaction product containing prenol prepared by the hydrogenation of β -methylcrotonaldehyde is distilled at 20 ~ 140°C under 1 ~ 760 mmHg, or preferably at 30 ~ 100°C under 3 ~ 200 mmHg.

Also, the reaction product containing geraniol prepared by the hydrogenation of citral is distilled at 50 ~ 200°C under 0.3 ~ 300 mmHg, or preferably at 70 ~ 180°C under 1 ~ 180 mmHg.

Any types of conventionally known apparatuses, for example, a tray-type, packing-type or thin film-type apparatus, can be used for distillation.

According to the present invention, a desired unsaturated alcohol can be obtained at a high yield.

Also, according to the present invention, an unsaturated alcohol can be obtained from an unsaturated aldehyde at a high degree of selectivity

and conversion. Also, the present invention has an advantage in that since the reaction product to be subjected to distillation contains a lower amount of unreacted unsaturated aldehyde which decreases the yield by reacting with a formed unsaturated alcohol, a high-purity unsaturated alcohol can be obtained at a high yield.

The above distillation operation can be carried out using a batch-method or a continuous method and preferably under an atmosphere of an inert gas, such as nitrogen, argon, helium and the like. Furthermore, during the distillation, conventionally known stabilizers, such as amine compounds, hydroquinones, weak acids and the like, can be added to prevent the degradation of the unsaturated aldehyde.

In the above sections, a preferred mode of carrying out the separation-purification of the unsaturated alcohol from the reaction product using a distillation operation has been explained. However, the present invention is not restricted to this method. Other separation-purification methods, such as chromatography, recrystallization and the like, can be employed.

According to the present invention, the unsaturated alcohol can be obtained from the corresponding unsaturated aldehyde at an extremely high degree of selectivity and conversion.

The present invention will be explained in more detail below.

Example 1-A

To a 500-cc autoclave equipped with an electromagnetically rotating stirrer, 0.5 parts of platinum oxide, 150 parts of 90% methanol, 0.375 parts

of ferrous sulfate heptahydrate and 0.0825 parts of zinc acetate dihydrate were charged. The interior of the autoclave was sufficiently substituted first with nitrogen, then with hydrogen. After introduction of hydrogen to a pressure of 10 kg/cm² G, the mixture was stirred at room temperature for 2 hours. At this point, the stirring was stopped and platinum oxide was separated by sedimentation. Sedimentation of platinum oxide was completed in 10 minutes. Then, sedimentation separation was repeated twice by adding 100 parts of 90% methanol each time to prepare a catalyst. A small amount of sample was taken from the obtained catalyst to analyze the characteristics of the catalyst, indicating that the catalyst had a surface area of 15.0 m²/g, Fe retention of 2.4 wt%, and Zn retention of 5.6 wt%. Subsequently, 0.4 parts of the obtained platinum oxide, 21 parts of β -methylcrotonaldehyde, 150 parts of 90% methanol, 0.0037 parts of ferrous sulfate heptahydrate and 0.0024 parts of zinc acetate dihydrate were charged into the above 500-cc autoclave. After the interior of the autoclave was sufficiently substituted first with nitrogen, then with hydrogen, hydrogen was introduced to the autoclave to a pressure of 30 kg/cm² G. The reaction was allowed to proceed for 6 hours under stirring while the pressure was maintained at 30 kg/cm² G. Then, stirring was stopped and the interior of the autoclave was substituted with nitrogen. The mixture was allowed to stand for 15 minutes.

Then, the supernatant liquid was slowly taken out from the mixture to obtain 153 parts of the reaction mixture. While platinum oxide was left in the autoclave, fresh β -methylcrotonaldehyde, 90% methanol,

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ferrous sulfate, and zinc acetate in the same mixing ratios as above were charged into the autoclave and the reaction was repeated. The obtained reaction mixture was colorless and transparent after each reaction cycle and contained platinum oxide, ferrous sulfate, and zinc acetate in amounts of, converted to metallic platinum, iron, and zinc, 1 ppm or less, 20 ~ 25 ppm, and 20 ~22 ppm, respectively, based on the sum of β -methylcrotonaldehyde and prenol in the reaction mixture. The results of the reaction are shown in Table 1.

A small amount of sample was taken from platinum oxide that remained in the autoclave to measure the particle size. The platinum oxide had an average particle size of 25 μ , which was much larger than the particle size of 2 μ for platinum oxide before the catalyst preparation.

The above reaction medium was introduced to a flask equipped with a packing-type rectification tower. After the removal of methanol under the reduced pressure of 200 mmHg abs, distillation of prenol was carried out under the reduced pressure of 50 mmHg abs. The degree of distillation recovery of prenol was 95%, while that of unreacted β -methylcrotonaldehyde was 94%. The degree of distillation recovery of each component is defined by the following formula.

The degree of distillation recovery = [(amount of each component in the distillate) + (amount of each component in the residual liquid in the flask)] x 100 / (amount of each component in the charged raw materials).

Table 1

Number of reaction cycle	Degree of conversion (%)	Degree of selectivity (%)		
		prenol	Isoamyl alcohol	isovaleraldehyde
1	75	95.0	3.5	1.5
10	76	94.8	3.6	1.6
20	74	95.5	3.4	1.1
30	73	94.2	3.7	1.1

Example 1-B

To the same autoclave used in Example 1 [sic.], 0.5 parts of platinum oxide prepared by following the same procedure as describe in Example 1-A, 21 parts of β -methylcrotonaldehyde and 150 parts of 90% methanol were charged and the reaction was allowed to proceed following the same procedure as described in Example 1 [sic.], except that ferrous sulfate heptahydrate and zinc acetate dihydrate were not used. The platinum oxide catalyst was repeatedly used for 8 cycles. The reaction mixture obtained after each reaction cycle was colorless and transparent and contained platinum oxide, ferrous sulfate and zinc acetate in amounts of, converted to metallic platinum, iron, and zinc, 1 ppm or less, 33 ppm, and 26.6 ppm, respectively, based on the sum of β -methylcrotonaldehyde and prenol. At the first reaction cycle, the degree of conversion of β -methylcrotonaldehyde was 74% and the degree of selectivity for prenol was 95.0%. At the 6th reaction cycle, the degree of conversion of β -methylcrotonaldehyde was 76% and the degree of selectivity for prenol was 91.0%. At the 8th reaction cycle, no change in the degree of conversion was observed, but the degree of selectivity for prenol was 88.0%.

Example 2

To a 500-cc autoclave equipped with an electromagnetically rotating stirrer, 0.5 parts of platinum oxide which was prepared following the same procedure as described in Example 1-A [sic.], 150 parts of 90% methanol, 0.375 parts of ferrous sulfate heptahydrate, and 0.0825 parts of zinc acetate dihydrate were charged and the catalyst was prepared following the same procedure as described in Example 1. A small amount of sample was taken from the obtained catalyst to analyze the characteristics of the catalyst, indicating that the catalyst had a surface area of $14.6 \text{ m}^2/\text{g}$, Fe retention of 2.6 wt%, and Zn retention of 5.6 wt%. Subsequently, the obtained platinum oxide [sic. Translator's comment: no amount given], 38 parts citral, 150 parts of 90% methanol, 0.0037 parts of ferrous sulfate heptahydrate and 0.0024 parts of zinc acetate dihydrate were charged into the above 500-cc autoclave. After the interior of the autoclave was sufficiently substituted with nitrogen and hydrogen, hydrogen was introduced to the autoclave to a pressure of $30 \text{ kg/cm}^2 \text{ G}$. The reaction was allowed to proceed for 6 hours under stirring while the pressure was maintained at $30 \text{ kg/cm}^2 \text{ G}$. Then, stirring was stopped and the interior of the autoclave was substituted with nitrogen. The mixture was allowed to stand for 15 minutes.

Then the supernatant liquid was slowly taken out from the mixture to obtain 170 parts of the reaction mixture. While platinum oxide was left in the autoclave, fresh citral, 90% methanol, ferrous sulfate heptahydrate, and zinc acetate dihydrate in the same mixing ratios as described above were charged into the autoclave and the reaction was repeated.

The obtained reaction mixture was colorless and transparent after each reaction cycle and contained platinum oxide, ferrous sulfate, and zinc acetate in amounts of, converted to metallic platinum, metallic iron, and metallic zinc, 1 ppm or less, 15 ~ 25 ppm, and 7 ~25 ppm, respectively, based on the sum of citral, geraniol and nerol in the reaction mixture. The results of the reaction are shown in Table 2.

The platinum oxide remained in the autoclave had an average particle size of 20 μ , which was much larger than the average particle size of 2 μ for the platinum oxide before the catalyst preparation. The above reaction mixture was introduced to a flask equipped with a rotary band-type rectification tower. After the removal of methanol under the reduced /10 pressure of 200 mmHg abs, distillation of geraniol was carried out under the reduced pressure of 5 mmHg abs. The degree of distillation recovery of geraniol was 94%, while that of unreacted citral was 93%. The degree of distillation recovery of each component has been already defined in Example 1-A.

Table 2

Number of reaction cycle	Degree of conversion (%)	Degree of selectivity (%)		
		geraniol,nerol	citronellol	others
1	70	94.5	3.2	2.3
10	72	93.0	3.1	3.9
20	69	94.0	3.3	2.7
30	71	95.1	3.0	1.9

Comparative Example 1

To the same 500-cc autoclave used in Example 1, 0.5 parts of platinum oxide, 38.0 parts of citral, 150 parts of 90% methanol, 0.375 parts of ferrous

sulfate heptahydrate and 0.0825 parts of zinc acetate dihydrate were charged. The interior of the autoclave was sufficiently substituted with nitrogen and hydrogen. After introduction of hydrogen to a pressure of 30 kg/cm² G, the reaction was allowed to proceed for 4 hours under mixing while the pressure was maintained at 30 kg/cm² G. At this point, stirring was stopped and the interior of the autoclave was substituted with nitrogen. The mixture was allowed to stand overnight. The reaction mixture and the catalyst were separated by slowly taking out 188 parts of the supernatant solution. A small amount of sample was taken from the separated catalyst to analyze the characteristics of the catalyst, indicating that the catalyst had a surface area of 6.8 m²/g, Fe retention of 5.2 wt%, and Zn retention of 5.7 wt%. The surface area of the catalyst was smaller than that of the catalyst obtained in Example 2. The above reaction mixture had a black color with almost no transparency. It contained platinum oxide, ferrous sulfate, and zinc acetate in amounts of, converted to metallic platinum, iron, and zinc, 140 ppm, 1,680 ppm, and 175 ppm, respectively, based on the sum of citral, geraniol, nerol, and citronellol. In the 1st reaction cycle, the degree of conversion of citral 72%, while the degree of selectivity for the corresponding unsaturated alcohols (geraniol and nerol) was 89%. The platinum oxide which remained in the autoclave had an average particle size of 2 μ which was the same as that of platinum oxide before catalyst preparation.

The above reaction mixture was introduced to a flask equipped with a rotary band-type rectification tower. After the removal of methanol under

the reduced pressure of 200 mmHg abs, distillation of geraniol was carried out under the reduced pressure of 5 mmHg abs. The degree of distillation recovery of geraniol was 67%, while that of unreacted citral was 120%. The amount of citral increased as compared to the initially charged amount. The degree of distillation recovery of each component has been already defined in Example 1-A.

Comparative Example 2

To the same 500-cc autoclave used in Example 1-A, 0.5 parts of platinum oxide and 150 parts of 90% methanol were charged. The interior of the autoclave was sufficiently substituted first with nitrogen, then with hydrogen. After introduction of hydrogen to a pressure of 10 kg/cm² G, the mixture was stirred for 2 hours while the pressure was maintained at 10 kg/cm² G. At this point, the stirring was stopped and platinum oxide was separated by sedimentation. Sedimentation of platinum oxide was completed in 30 minutes. Then, sedimentation separation was repeated twice by adding 100 parts of 90% methanol each time to prepare a catalyst. A small amount of sample was taken from the obtained catalyst to analyze the characteristics of the catalyst, indicating that the catalyst had a surface area of 30 m²/g, Fe retention of 0.4 wt%, and Zn retention of 0 wt%. The presence of a trace amount of Fe on the catalyst was considered to be due to the fact that 90% methanol, used as the solvent, contained dissolved iron. Subsequently, the obtained platinum oxide [sic. Translator's comment: no amount given], 21 parts of β -methylcrotonaldehyde and 150 parts of 90% methanol were charged into the above 500-cc autoclave. After the

interior of the autoclave was sufficiently substituted first with nitrogen, then with hydrogen, hydrogen was introduced to the autoclave to a pressure of 30 kg/cm² G. The reaction was allowed to proceed for 6 hours under stirring while the pressure was maintained at 30 kg/cm² G. Then, the mixture was allowed to stand for 30 minutes to separate the catalyst from the reaction mixture by sedimentation. The amount of the obtained reaction mixture was 150 parts.

The degree of conversion of β -methylcrotonaldehyde was 60.6%, while the degree of selectivity for prenol was 3.8%. In addition, isovaleraldehyde and isoamyl alcohol were formed.

Comparative Example 3

To the same 500-cc autoclave used in Example 1-A, 0.5 parts of platinum oxide and 150 parts of 90% methanol were charged. The interior of the autoclave was sufficiently substituted first with nitrogen, then with hydrogen. After introduction of hydrogen to a pressure of 10 kg/cm² G, the mixture was stirred for 1 hour while the pressure was maintained at 10 kg/cm² G. At this point, the stirring was stopped and the mixture was allowed to stand for 30 minutes to separate platinum oxide by sedimentation. After the supernatant liquid was slowly removed, 0.375 parts of ferrous /11 sulfate heptahydrate, 0.0825 parts of zinc acetate dehydrate, and 150 parts of 90% methanol were added. The interior of the autoclave was again sufficiently substituted with nitrogen and hydrogen. Then, hydrogen was introduced to a pressure of 10 kg/cm² G and the mixture was stirred for 1 hour while the pressure was maintained at 10 kg/cm² G. Then, the stirring

was stopped and the mixture was allowed to stand for 30 minutes to separate platinum oxide by sedimentation. Furthermore, sedimentation separation was repeated twice by adding 100 parts of 90% methanol each time to prepare a catalyst. A small amount of sample was taken from the obtained catalyst to analyze the characteristics of the catalyst, indicating that the catalyst had a surface area of $14.6 \text{ m}^2/\text{g}$, Fe retention of 0.7 wt%, and Zn retention of 3 wt%. Subsequently, the obtained platinum oxide [sic. Translator's comment: no amount given], 38 parts of citral and 150 parts of 90% methanol were charged into the above 500-cc autoclave. After the interior of the autoclave was sufficiently substituted first with nitrogen, then with hydrogen, hydrogen was introduced to the autoclave to a pressure of $30 \text{ kg/cm}^2 \text{ G}$. The reaction was allowed to proceed for 6 hours under stirring while the pressure of hydrogen was maintained at $30 \text{ kg/cm}^2 \text{ G}$. Then, the mixture was allowed to stand for 30 minutes to separate the catalyst from the reaction mixture by sedimentation. The amount of the obtained reaction mixture was 168 parts. The degree of conversion of citral was 23.8%, while the degree of selectivity for geraniol and nerol was 54.2%. In addition, citronellol, 2,6-dimethyloctanol and citronellal were obtained.

Example 3

To a 100-cc autoclave which was a similar type as described in Example 1-A, 0.1 parts of platinum oxide, 30 parts of 90% methanol and 0.075 parts of ferrous sulfate heptahydrate were charged. The interior of the autoclave was substituted with nitrogen. After introduction of hydrogen to a pressure of $10 \text{ kg/cm}^2 \text{ G}$, the mixture was stirred at room temperature for 1 hour. At

this point, the stirring was stopped and the mixture was allowed to stand for 30 minutes to separate platinum oxide by sedimentation. After the supernatant solution was slowly removed, 0.011 parts of zinc acetate dihydrate and 30 parts of 90% methanol were added. Interior of the autoclave was again substituted with nitrogen and hydrogen. Then, hydrogen was introduced to a pressure of 10 kg/cm² G. The mixture was stirred for 1 hour while the pressure was maintained at 10 kg/cm² G. At this point, stirring was stopped and the mixture was allowed to stand for 30 minutes to separate platinum oxide by sedimentation. This sedimentation separation was repeated twice by adding 20 parts of 90% methanol each time. A small amount of sample was taken from the obtained catalyst to analyze the characteristics of the catalyst, indicating that the catalyst had a surface area of 18.5 m²/g, Fe retention of 4.3 wt%, and Zn retention of 5.5 wt%. Subsequently, the obtained platinum oxide [sic. Translators comment: no amount given], 7.6 parts of citral and 30 parts of 90% methanol were charged into the above 100-cc autoclave. After the interior of the autoclave was sufficiently substituted first with nitrogen, then with hydrogen, hydrogen was introduced to the autoclave to a pressure of 30 kg/cm² G. The reaction was allowed to proceed for 4 hours under stirring while the pressure was maintained at 30 kg/cm² G. Then, the mixture was allowed to stand for 30 minutes to obtain 37 parts of the reaction mixture after the catalyst was separated by sedimentation.

The degree of conversion of citral was 56%, while the degree of selectivity for geraniol and nerol was 91.7%. In addition, citronellol was obtained.

Example 4

To the same 100-cc autoclave used in Example 3, 0.1 parts of platinum oxide, 30 parts of 90% methanol and 0.011 parts of zinc acetate dihydrate were charged. The interior of the autoclave was sufficiently substituted with nitrogen then with hydrogen. After introduction of hydrogen to a pressure of 10 kg/cm² G, the mixture was stirred at room temperature for 1 hour. At this point, the stirring was stopped and the mixture was allowed to stand for 30 minutes to separate platinum oxide by sedimentation. After the supernatant solution was slowly removed, 0.075 parts of ferrous sulfate heptahydrate and 30 parts of 90% methanol were added. Interior of the autoclave was again substituted sufficiently with nitrogen and hydrogen. Then, hydrogen was introduced to a pressure of 10 kg/cm² G. The mixture was stirred for 1 hour while the pressure was maintained at 10 kg/cm² G. At this point, stirring was stopped and the mixture was allowed to stand for 30 minutes to separate platinum oxide by sedimentation. This sedimentation separation was repeated twice by adding 20 parts of 90% methanol each time. A small amount of sample was taken from the obtained catalyst to analyze the characteristics of the catalyst, indicating that the catalyst had a surface area of 19.4 m²/g, Fe retention of 2.5 wt%, and Zn retention of 5.0 wt%. Subsequently, the obtained platinum oxide [sic. Translators comment: no amount given], 7.6 parts of citral and 30 parts of 90% methanol were charged into the above 100-cc autoclave. After the interior of the autoclave was sufficiently substituted with nitrogen and hydrogen, hydrogen was introduced to the autoclave to a pressure of 30

kg/cm² G. The reaction was allowed to proceed for 4 hours under mixing while the pressure was maintained at 30 kg/cm² G. Then, the mixture was allowed to stand for 30 minutes to obtain 37 parts of the reaction mixture after the catalyst was separated by sedimentation.

The degree of conversion of citral was 66.2%, while the degree of selectivity for geraniol and nerol was 91.9%. In addition, citronellol was obtained.

Comparative Example 4

To the same 500-cc autoclave used in Example 1-A, 0.5 parts of platinum black, 150 parts of 90% methanol, 0.375 parts of ferrous sulfate heptahydrate and 0.055 parts of zinc acetate dihydrate were charged. The interior /12 of the autoclave was sufficiently substituted with nitrogen, then with hydrogen. After introduction of hydrogen to a pressure of 10 kg/cm² G, the mixture was stirred at room temperature for 1 hour. At this point, the stirring was stopped and the catalyst was separated by sedimentation. In 35 minutes, a majority of platinum black was settled. The supernatant solution having a slightly black color was slowly removed and the sedimentation separation was repeated twice by adding 100 parts of 90% methanol each time. A small amount of sample was taken from the separated catalyst to analyze the characteristics of the catalyst, indicating that the catalyst had a surface area of 30.5 m²/g, Fe retention of 1 wt%, and Zn retention of 3.3 wt%. To the above 500-cc autoclave, the above platinum black catalyst [sic. Translator's comment: no amount given], 38 parts of citral and 150 parts of 90% methanol were charged. After the interior of

the autoclave was sufficiently substituted with nitrogen and hydrogen, hydrogen was introduced to a pressure of 30 kg/cm² G and the reaction was allowed to proceed for 4 hours under mixing while the pressure was maintained at 30 kg/cm² G. Then, the mixture was allowed to stand for 40 minutes to obtain 185 parts of reaction mixture after separation of the catalyst by sedimentation. The degree of conversion of citral was 7.0%, while the degree of selectivity for geraniol and nerol was 67%, giving poor result.

Comparative Example 5

To the same 500-cc autoclave used in Example 1-A, 0.5 parts of platinum oxide, 150 parts of 90% methanol, 0.0695 parts of ferrous sulfate heptahydrate, 0.0658 parts of zinc acetate dihydrate and 38 parts of citral were charged. The interior of the autoclave was sufficiently substituted with nitrogen, then with hydrogen. After introduction of hydrogen to a pressure of 30 kg/cm² G, the mixture was stirred at room temperature for 4 hours. At this point, the stirring was stopped and the catalyst was separated by sedimentation. In 20 minutes, a majority of platinum oxide was settled. The supernatant solution having a slightly black color was taken out to obtain 188 parts of the reaction mixture and the catalyst. A small amount of sample was taken from the separated catalyst to analyze the characteristics of the catalyst, indicating that the catalyst had a surface area of 6.6 m²/g, Fe retention of 1.1 wt%, and Zn retention of 8.1 wt%. When the reaction mixture was analyzed, the degree of conversion of citral was 70%, while the degree of selectivity for geraniol and nerol was

79%. Compared to the results of Example 1, the degree of selectivity was lower and the catalyst had a smaller surface area.

Comparative Example 6

To the same 100-cc autoclave used in Example 3, 0.1 parts of platinum oxide, 30 parts of 90% methanol, 0.18 parts of ferrous sulfate heptahydrate and 0.04 parts of zinc acetate dihydrate were charged. The interior of the autoclave was sufficiently substituted with nitrogen, then with hydrogen. After introduction of hydrogen to a pressure of 10 kg/cm² G, the mixture was stirred at room temperature for 1 hour. At this point, the stirring was stopped and platinum oxide was separated by sedimentation. The sedimentation separation was repeated twice by adding 20 parts of 90% methanol each time to obtain the catalyst.

A small amount of sample was taken from the obtained catalyst to analyze the characteristics of the catalyst, indicating that the catalyst had a surface area of 17.6 m²/g, Fe retention of 3.7 wt%, and Zn retention of 9.7 wt%. To the above 100-cc autoclave, the obtained platinum oxide [sic. Translator's comment: no amount given], 7.6 parts of citral and 30 parts of 90% methanol were charged. After the interior of the autoclave was sufficiently substituted with nitrogen and hydrogen, hydrogen was introduced to a pressure of 30 kg/cm² G and the reaction was allowed to proceed for 4 hours under stirring while the pressure was maintained at 30 kg/cm² G. Then, stirring was stopped and the interior of the autoclave was substituted with nitrogen. The mixture was allowed to stand for 15 minutes.

By slowly taking out the supernatant solution, 37.6 parts of reaction mixture was obtained. The degree of conversion of citral was 10.7%, while the degree of selectivity for geraniol and nerol was 60%.

Comparative Example 7

To the same 100-cc autoclave used in Example 3, 0.1 parts of platinum oxide, 30 parts of 90% methanol, 0.018 parts of ferrous sulfate heptahydrate and 0.011 parts of zinc acetate dihydrate were charged. The interior of the autoclave was sufficiently substituted with nitrogen, then with hydrogen. After introduction of hydrogen to a pressure of 10 kg/cm² G, the mixture was stirred at room temperature for 1 hour. At this point, the stirring was stopped and platinum oxide was separated by sedimentation. The sedimentation separation was repeated twice by adding 20 parts of 90% methanol each time to obtain the catalyst.

A small amount of sample was taken from the obtained catalyst to analyze the characteristics of the catalyst, indicating that the catalyst had a surface area of 13.5 m²/g, Fe retention of 0.6 wt%, and Zn retention of 5.7 wt%. To the above 100-cc autoclave, the obtained platinum oxide [sic. Translator's comment: no amount given], 7.6 parts of citral and 30 parts of 90% methanol were charged. After the interior of the autoclave was sufficiently substituted with nitrogen and hydrogen, hydrogen was introduced to a pressure of 30 kg/cm² G and the reaction was allowed to proceed for 4 hours under stirring while the pressure was maintained at 30 kg/cm² G. Then, stirring was stopped and the interior of the autoclave was substituted with nitrogen. The mixture was allowed to stand for 15

/13

minutes.

By slowly taking out the supernatant solution, 37.6 parts of reaction mixture was obtained. The degree of conversion of citral was 31.8%, while the degree of selectivity for geraniol and nerol was 73%.

Comparative Example 8

To the same 100-cc autoclave used in Example 3, 0.1 parts of platinum oxide, 30 parts of 90% methanol, 0.045 parts of ferrous sulfate heptahydrate and 0.045 parts of zinc acetate dihydrate were charged. The interior of the autoclave was sufficiently substituted with nitrogen, then with hydrogen. After introduction of hydrogen to a pressure of 10 kg/cm² G, the mixture was stirred at room temperature for 1 hour. At this point, the stirring was stopped and platinum oxide was separated by sedimentation. The sedimentation separation was repeated twice by adding 20 parts of 90% methanol each time to obtain the catalyst.

A small amount of sample was taken from the obtained catalyst to analyze the characteristics of the catalyst, indicating that the catalyst had a surface area of 16.2 m²/g, Fe retention of 1.7 wt%, and Zn retention of 10.6 wt%. To the above 100-cc autoclave, the obtained platinum oxide [sic. Translator's comment: no amount given], 7.6 parts of citral and 30 parts of 90% methanol were charged. After the interior of the autoclave was sufficiently substituted with nitrogen and hydrogen, hydrogen was introduced to a pressure of 30 kg/cm² G and the reaction was allowed to proceed for 4 hours under stirring while the pressure was maintained at 30 kg/cm²

G. Then, stirring was stopped and the interior of the autoclave was substituted with nitrogen. The mixture was allowed to stand for 15 minutes.

By slowly taking out the supernatant solution, 37.6 parts of reaction mixture was obtained. The degree of conversion of citral was 15.0%, while the degree of selectivity for geraniol and nerol was 64.8%.

Comparative Example 9

To the same 100-cc autoclave used in Example 3, 0.1 parts of platinum oxide, 30 parts of 90% methanol and 0.10 parts of ferrous sulfate heptahydrate were charged. The interior of the autoclave was sufficiently substituted with nitrogen, then with hydrogen. After introduction of hydrogen to a pressure of 10 kg/cm² G, the mixture was stirred at room temperature for 1 hour. At this point, the stirring was stopped and platinum oxide was separated by sedimentation. The sedimentation separation was repeated twice by adding 20 parts of 90% methanol each time to obtain the catalyst.

A small amount of sample was taken from the obtained catalyst to analyze the characteristics of the catalyst, indicating that the catalyst had a surface area of 18.5 m²/g, Fe retention of 4.4 wt%, and Zn retention of 0 wt%. To the above 100-cc autoclave, the obtained platinum oxide [sic. Translator's comment: no amount given], 7.6 parts of citral and 30 parts of 90% methanol were charged. After the interior of the autoclave was sufficiently substituted with nitrogen and hydrogen, hydrogen was introduced to a pressure of 30 kg/cm² G and the reaction was allowed to proceed for 4 hours under stirring while the pressure was maintained at 30 kg/cm²

G. Then, stirring was stopped and the interior of the autoclave was substituted with nitrogen. The mixture was allowed to stand for 15 minutes.

By slowly taking out the supernatant solution, 37.6 parts of reaction mixture was obtained. The degree of conversion of citral was 76.0%, while the degree of selectivity for geraniol and nerol was 75.5%.

Example 5

To the same 100-cc autoclave used in Example 3, 0.1 parts of platinum oxide, 30 parts of 85% methanol, 0.05 parts of ferrous sulfate heptahydrate and 0.01 parts of zinc acetate dihydrate were charged. The interior of the autoclave was sufficiently substituted with nitrogen, then with hydrogen. After introduction of hydrogen to a pressure of 10 kg/cm² G, the mixture was stirred at room temperature for 1 hour. At this point, the stirring was stopped and platinum oxide was separated by sedimentation. The sedimentation separation was repeated twice by adding 20 parts of 85% methanol each time to obtain the catalyst.

A small amount of sample was taken from the obtained catalyst to analyze the characteristics of the catalyst, indicating that the catalyst had a surface area of 13.2 m²/g, Fe retention of 1.5 wt%, and Zn retention of 5.3 wt%. To the above 100-cc autoclave, the obtained platinum oxide [sic. Translator's comment: no amount given], 7.6 parts of citral and 30 parts of 90% methanol were charged. After the interior of the autoclave was sufficiently substituted with nitrogen and hydrogen, hydrogen was introduced to a pressure of 30 kg/cm² G and the reaction was allowed to proceed for 4 hours under stirring while the pressure was maintained at 30 kg/cm²

G. Then, stirring was stopped and the interior of the autoclave was substituted with nitrogen. The mixture was allowed to stand for 15 minutes.

By slowly taking out the supernatant solution, 37.6 parts of reaction mixture was obtained. The degree of conversion of citral was 76.7%, while the degree of selectivity for geraniol and nerol was 93%.

Example 6

To the same 100-cc autoclave used in Example 3, 0.1 parts of platinum oxide, 30 parts of methanol, 0.18 parts of ferrous sulfate heptahydrate and 0.01 parts of zinc acetate dihydrate were charged. The interior of the autoclave was sufficiently substituted with nitrogen, then with hydrogen. After introduction of hydrogen to a pressure of 10 kg/cm² G, the mixture was stirred at room temperature for 1 hour. At this point, the stirring was stopped and platinum oxide was separated by sedimentation. The sedimentation separation was repeated twice by adding 20 parts of /14 methanol each time to obtain the catalyst.

A small amount of sample was taken from the obtained catalyst to analyze the characteristics of the catalyst, indicating that the catalyst had a surface area of 15.6 m²/g, Fe retention of 43.6 wt%, and Zn retention of 5.0 wt%. To the above 100-cc autoclave, the obtained platinum oxide [sic. Translator's comment: no amount given], 7.6 parts of citral and 30 parts of 90% methanol were charged. After the interior of the autoclave was sufficiently substituted with nitrogen and hydrogen, hydrogen was introduced to a pressure of 30 kg/cm² G and the reaction was allowed to proceed for 4 hours under stirring while the pressure was maintained at 30 kg/cm²

G. Then, stirring was stopped and the interior of the autoclave was substituted with nitrogen. The mixture was allowed to stand for 15 minutes.

By slowly taking out the supernatant solution, 37.6 parts of reaction mixture was obtained. The degree of conversion of citral was 70.5%, while the degree of selectivity for geraniol and nerol was 91.4%.

Example 7

To the same 100-cc autoclave used in Example 3, 0.1 parts of platinum oxide, 30 parts of 80% methanol, 0.1 parts of ferrous sulfate heptahydrate and 0.011 parts of zinc acetate dihydrate were charged. The interior of the autoclave was sufficiently substituted with nitrogen, then with hydrogen. After introduction of hydrogen to a pressure of 10 kg/cm² G, the mixture was stirred at room temperature for 1 hour. At this point, the stirring was stopped and platinum oxide was separated by sedimentation. The sedimentation separation was repeated twice by adding 20 parts of 80% methanol each time to obtain the catalyst.

A small amount of sample was taken from the obtained catalyst to analyze the characteristics of the catalyst, indicating that the catalyst had a surface area of 37.6 m²/g, Fe retention of 4.6 wt%, and Zn retention of 5.6 wt%. To the above 100-cc autoclave, the obtained platinum oxide [sic. Translator's comment: no amount given], 7.6 parts of citral and 30 parts of 85% methanol were charged. After the interior of the autoclave was sufficiently substituted with nitrogen and hydrogen, hydrogen was introduced to a pressure of 30 kg/cm² G and the reaction was allowed to proceed for 4 hours under stirring while the pressure was maintained at 30 kg/cm²

G. Then, stirring was stopped and the interior of the autoclave was substituted with nitrogen. The mixture was allowed to stand for 15 minutes.

By slowly taking out the supernatant solution, 37.6 parts of reaction mixture was obtained. The degree of conversion of citral was 84.6%, while the degree of selectivity for geraniol and nerol was 92.8%.

Example 8

To the same 100-cc autoclave used in Example 3, 0.1 parts of platinum oxide, 30 parts of 87% methanol, 0.075 parts of ferrous sulfate heptahydrate and 0.004 parts of zinc acetate dihydrate were charged. The interior of the autoclave was sufficiently substituted with nitrogen, then with hydrogen. After introduction of hydrogen to a pressure of 10 kg/cm² G, the mixture was stirred at room temperature for 1 hour. At this point, the stirring was stopped and platinum oxide was separated by sedimentation. The sedimentation separation was repeated twice by adding 20 parts of 87% methanol each time to obtain the catalyst.

A small amount of sample was taken from the obtained catalyst to analyze the characteristics of the catalyst, indicating that the catalyst had a surface area of 15.7 m²/g, Fe retention of 2.7 wt%, and Zn retention of 2.3 wt%. To the above 100-cc autoclave, the obtained platinum oxide [sic. Translator's comment: no amount given], 7.6 parts of citral and 30 parts of 92% methanol were charged. After the interior of the autoclave was sufficiently substituted with nitrogen and hydrogen, hydrogen was introduced to a pressure of 30 kg/cm² G and the reaction was allowed to proceed for 4 hours under stirring while the pressure was maintained at 30 kg/cm²

G. Then, stirring was stopped and the interior of the autoclave was substituted with nitrogen. The mixture was allowed to stand for 15 minutes.

By slowly taking out the supernatant solution, 37.6 parts of reaction mixture was obtained. The degree of conversion of citral was 77.2%, while the degree of selectivity for geraniol and nerol was 88.1%.

Example 9

To the same 100-cc autoclave used in Example 3, 0.1 parts of platinum oxide, 30 parts of 90% ethanol, 0.12 parts of ferrous sulfate heptahydrate and 0.002 parts of zinc acetate dihydrate were charged. The interior of the autoclave was sufficiently substituted with nitrogen, then with hydrogen. After introduction of hydrogen to a pressure of 10 kg/cm² G, the mixture was stirred at room temperature for 1 hour. At this point, the stirring was stopped and platinum oxide was separated by sedimentation. The sedimentation separation was repeated twice by adding 20 parts of 90% ethanol each time to obtain the catalyst.

A small amount of sample was taken from the obtained catalyst to analyze the characteristics of the catalyst, indicating that the catalyst had a surface area of 14.3 m²/g, Fe retention of 12 wt%, and Zn retention of 0.9 wt%. To the above 100-cc autoclave, the obtained platinum oxide [sic. Translator's comment: no amount given], 7.6 parts of citral and 30 parts of 90% ethanol were charged. After the interior of the autoclave was sufficiently substituted with nitrogen and hydrogen, hydrogen was introduced to a pressure of 30 kg/cm² G and the reaction was allowed to proceed for 4 hours under stirring while the pressure was maintained at 30 kg/cm²

G. Then, stirring was stopped and the interior of the autoclave was substituted with nitrogen. The mixture was allowed to stand for 15 minutes.

By slowly taking out the supernatant solution, 37.6 parts of reaction mixture was obtained. The degree of conversion of citral was 80.1%, /15 while the degree of selectivity for geraniol and nerol was 85%.

Example 10

To the same 100-cc autoclave used in Example 3, 0.1 parts of platinum oxide, 30 parts of 95% ethanol, 0.12 parts of ferrous sulfate heptahydrate and 0.005 parts of zinc acetate dihydrate were charged. The interior of the autoclave was sufficiently substituted with nitrogen, then with hydrogen. After introduction of hydrogen to a pressure of 10 kg/cm² G, the mixture was stirred at room temperature for 1 hour. At this point, the stirring was stopped and platinum oxide was separated by sedimentation. The sedimentation separation was repeated twice by adding 20 parts of 95% ethanol each time to obtain the catalyst.

A small amount of sample was taken from the obtained catalyst to analyze the characteristics of the catalyst, indicating that the catalyst had a surface area of 15.3 m²/g, Fe retention of 11.8 wt%, and Zn retention of 2.8 wt%. To the above 100-cc autoclave, the obtained platinum oxide [sic. Translator's comment: no amount given], 7.6 parts of citral and 30 parts of 95% ethanol were charged. After the interior of the autoclave was sufficiently substituted with nitrogen and hydrogen, hydrogen was introduced to a pressure of 30 kg/cm² G and the reaction was allowed to proceed for 4 hours under stirring while the pressure was maintained at 30 kg/cm²

G. Then, stirring was stopped and the interior of the autoclave was substituted with nitrogen. The mixture was allowed to stand for 15 minutes.

By slowly taking out the supernatant solution, 37.6 parts of reaction mixture was obtained. The degree of conversion of citral was 83.2%, while the degree of selectivity for geraniol and nerol was 96.6%.

Example 11

To the same 100-cc autoclave used in Example 3, 0.1 parts of platinum oxide, 30 parts of 95% methanol, 0.12 parts of ferrous sulfate heptahydrate and 0.01 parts of zinc acetate dihydrate were charged. The interior of the autoclave was sufficiently substituted with nitrogen, then with hydrogen. After introduction of hydrogen to a pressure of 10 kg/cm² G, the mixture was stirred at room temperature for 1 hour. At this point, the stirring was stopped and platinum oxide was separated by sedimentation. The sedimentation separation was repeated twice by adding 20 parts of 95% methanol each time to obtain the catalyst.

A small amount of sample was taken from the obtained catalyst to analyze the characteristics of the catalyst, indicating that the catalyst had a surface area of 33 m²/g, Fe retention of 11.6 wt%, and Zn retention of 4.7 wt%. To the above 100-cc autoclave, the obtained platinum oxide [sic. Translator's comment: no amount given], 7.6 parts of citral and 30 parts of 95% methanol were charged. After the interior of the autoclave was sufficiently substituted with nitrogen and hydrogen, hydrogen was introduced to a pressure of 30 kg/cm² G and the reaction was allowed to proceed for 4 hours under stirring while the pressure was maintained at 30 kg/cm²

G. Then, stirring was stopped and the interior of the autoclave was substituted with nitrogen. The mixture was allowed to stand for 15 minutes.

By slowly taking out the supernatant solution, 37.6 parts of reaction mixture was obtained. The degree of conversion of citral was 79.0%, while the degree of selectivity for geraniol and nerol was 97%.

Example 12

To the same 100-cc autoclave used in Example 3, 0.1 parts of platinum oxide, 30 parts of 90% methanol, 0.075 parts of ferrous sulfate heptahydrate and 0.011 parts of zinc acetate dihydrate were charged. The interior of the autoclave was sufficiently substituted with nitrogen, then with hydrogen. After introduction of hydrogen to a pressure of 10 kg/cm² G, the mixture was stirred at room temperature for 1 hour. At this point, the stirring was stopped and platinum oxide was separated by sedimentation. The sedimentation separation was repeated twice by adding 20 parts of 90% methanol each time to obtain the catalyst.

A small amount of sample was taken from the obtained catalyst to analyze the characteristics of the catalyst, indicating that the catalyst had a surface area of 14.7 m²/g, Fe retention of 2.4 wt%, and Zn retention of 5.6 wt%. To the above 100-cc autoclave, the obtained platinum oxide [sic. Translator's comment: no amount given], 6.6 parts of cinnamaldehyde and 30 parts of 90% methanol were charged. After the interior of the autoclave was sufficiently substituted with nitrogen and hydrogen, hydrogen was introduced to a pressure of 30 kg/cm² G and the reaction was allowed to proceed for 4 hours under stirring while the pressure was maintained at 30 kg/cm²

G. Then, stirring was stopped and the interior of the autoclave was substituted with nitrogen. The mixture was allowed to stand for 15 minutes.

By slowly taking out the supernatant solution, 37.6 parts of reaction mixture was obtained. The degree of conversion of cinnamaldehyde was 88.3%, while the degree of selectivity for cinnamyl alcohol was 100%.

Example 13

To the same 100-cc autoclave used in Example 3, 0.1 parts of platinum oxide, 30 parts of 90% methanol, 0.075 parts of ferrous sulfate heptahydrate and 0.011 parts of zinc acetate dihydrate were charged. The interior of the autoclave was sufficiently substituted with nitrogen, then with hydrogen. After introduction of hydrogen to a pressure of 10 kg/cm² G, the mixture was stirred at room temperature for 1 hour. At this point, the stirring was stopped and platinum oxide was separated by sedimentation. The sedimentation separation was repeated twice by adding 20 parts of /16 90% methanol each time to obtain the catalyst.

A small amount of sample was taken from the obtained catalyst to analyze the characteristics of the catalyst, indicating that the catalyst had a surface area of 14.7 m²/g, Fe retention of 2.4 wt%, and Zn retention of 5.6 wt%. To the above 100-cc autoclave, the obtained platinum oxide [sic. Translator's comment: no amount given], 5.0 parts of trans-2-hexenyl aldehyde and 30 parts of 90% methanol were charged. After the interior of the autoclave was sufficiently substituted with nitrogen and hydrogen, hydrogen was introduced to a pressure of 30 kg/cm² G and the reaction was allowed to proceed for 4 hours under stirring while the pressure was

maintained at 30 kg/cm² G. Then, stirring was stopped and the interior of the autoclave was substituted with nitrogen. The mixture was allowed to stand for 15 minutes.

By slowly taking out the supernatant solution, 37.6 parts of reaction mixture was obtained. The degree of conversion of trans-2-hexenyl aldehyde was 85.0%, while the degree of selectivity for trans-2-hexenyl alcohol was 83.1%.